Theoretical Elastic Moduli and Conformations of Polymer Chains

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ABSTRACT: A new method of calculation of the elastic moduli of single chains has been derived by using the equations of helical parameters under the condition that the rotation angle around the chain axis θ per one monomeric unit is kept constant ($\Delta\theta = 0$), when the chain is subjected to a homogeneous deformation. The importance of this condition has been confirmed from the good agreement between the calculated and observed moduli. The distribution of strain energy to the internal displacement coordinates (potential energy distributions (PED)) has been calculated under the condition of $\Delta\theta = 0$, in relation to the chain conformations. It has also been found that (1) PED is approximately proportional to $(\partial d/\partial R_i)^2$ and inversely proportional to F_{ii} and (2) the elastic moduli are mainly governed by $(\partial d/\partial R_i)^2 F_{ii}^{-1}$ for the internal coordinates having large PED, where d, R_i, and F_{ii} are the helical pitch, the ith internal coordinate, and the diagonal force constant for R_i, respectively. Discussion is made on several examples, such as isotactic polypropylene, poly(vinylidene fluoride), etc.

Crystallite modulus is one of the properties closely related to the crystal structures of polymers and seems to be basically important to the mechanical properties of crystalline polymers. The methods of calculation of the elastic moduli of polymer chains have been proposed by many investigators.[1-9] These methods may be classified into two kinds according to an additional condition: whether or not the rotation angle per one monomeric unit about the chain axis θ is kept constant ($\Delta\theta = 0$) when a polymer crystal is subjected to a homogeneous deformation. Treloar[4] and Shimanouchi et al.[5-7] calculated the elastic moduli of single chains without considering the condition of $\Delta\theta = 0$. Sugeta and Miyazawa[8] pointed out that the condition is necessary for preserving the translational symmetry of the three-dimensional crystal lattice and developed the method of calculation of the moduli by utilizing the **B** matrices frequently used in the normal coordinate treatments. We derived a new method of calculating the crystallite moduli under the condition $\Delta\theta = 0$. Here we also discuss the potential energy distributions to the internal displacement coordinates, i.e., the changes of the bond lengths, bond angles, and internal rotation angles, when the chain is stretched.

Basic Theory

The elastic modulus in the direction of chain axis E can be calulated as follows;

$$E = fd/(A\Delta d) \tag{1}$$

where Δd is the change of helical pitch d per one monomeric unit by the tensile force f, and A is the effective cross-sectional area of the chain.

The rotation angle θ and the pitch d of helical chain can be generally expressed in terms of the internal coordinates R_i.[10]

$$d = d(R_1, R_2, \ldots) \tag{2}$$

$$\theta = \theta(R_1, R_2, \ldots) \tag{3}$$

From eq 2, we have

$$\Delta d = \sum_i \frac{\partial d}{\partial R_i}\Delta R_i \tag{4}$$

By substituting the condition of $\Delta\theta = 0$ into eq 3, we obtain

$$\Delta\theta = 0 = \sum_i \frac{\partial\theta}{\partial R_i}\Delta R_i \tag{5}$$

The potential energy V is expressed as follows.

$$V = \tfrac{1}{2}\left(\sum_j F_{jj}\Delta R_j^2 + 2\sum_{k\neq j}\sum F_{jk}\Delta R_j \Delta R_k\right) \tag{6}$$

Here F_{jk} is the force constant associated with the kth and jth coordinates. The second and higher terms in eq 4 and 5 and the third and higher terms in eq 6 are neglected for simplicity. Since one of the internal coordinates is dependent upon the others under the condition of eq 5, the following equation is obtained for the ith internal coordinate.

$$\frac{\partial V}{\partial R_i} + \frac{\partial V}{\partial R_n}\frac{\partial R_n}{\partial R_i} = \frac{\partial V}{\partial d}\left(\frac{\partial d}{\partial R_i} + \frac{\partial d}{\partial R_n}\frac{\partial R_n}{\partial R_i}\right) \tag{7}$$

where $i = 1, 2, \ldots, n - 1$ (n is the number of all internal coordinates considered) and R_n is the dependent coordinate. Since we must also consider the redundant conditions, e.g., concerning the six bond angles around the tetrahedral carbon atom, the number of the dependent coordinates can be more than one. Hence eq 7 may be written in more general form as follows.

$$\sum_j \frac{\partial V}{\partial R_j}\frac{\partial R_j}{\partial R_i} = \frac{\partial V}{\partial d}\sum_j \frac{\partial d}{\partial R_j}\frac{\partial R_j}{\partial R_i} \tag{8}$$

where $i = 1, 2, \ldots, q$ and q is the number of the independent variables. From eq 6 and 8 we have

$$\sum_j \left(F_{jj}\Delta R_j + \sum_{k\neq j} F_{jk}\Delta R_k\right)\frac{\partial R_j}{\partial R_i} = f\sum_j \frac{\partial d}{\partial R_j}\frac{\partial R_j}{\partial R_i} \tag{9}$$

where $\partial V/\partial d = f$ = tensile force. The set of eq 5 and 9 and the redundant conditions is a system of simultaneous equations to all ΔR_i. Δd in eq 4 is calculated by using ΔR_i thus obtained, and then the modulus E can be given in eq 1.

The potential energy distributions (PED), i.e., the distributions (%) of strain energy to the internal displacement coordinates under stretching, are defined as follows. For the ith internal displacement coordinate ΔR_i,

$$(\text{PED})_i = 100F_{ii}\Delta R_i^2 \Big/ \sum_i F_{ii}\Delta R_i^2 \tag{10}$$

where F_{ii} is the diagonal term for ΔR_i of the symmetrized force constant matrix.

$(\text{-A-})_n$ Type Helices

In this case, the relationship between the internal coordinates and the helical parameters given in the general form by eq 2 and 3 is expressed as[10]

$$d\sin\frac{\theta}{2} = r\sin\frac{\phi}{2}\sin\frac{\tau}{2} \tag{11}$$

$$\cos\frac{\theta}{2} = \cos\frac{\tau}{2}\sin\frac{\phi}{2} \tag{12}$$

where r is the bond length, ϕ is the bond angle, and τ is the internal rotation angle (see Figure 1).

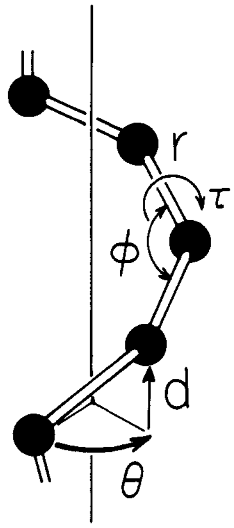


Figure 1. Helical parameters and internal coordinates of (-A-)$_n$ type helix.

Under the condition of $\Delta\theta = 0$, we can obtain $\partial d/\partial R_i$ in eq 4 from eq 11.

$$\frac{\partial d}{\partial r} = \frac{d}{r}, \quad \frac{\partial d}{\partial \phi} = \frac{d}{2}\cot\frac{\phi}{2}, \quad \frac{\partial d}{\partial \tau} = \frac{d}{2}\cot\frac{\tau}{2} \tag{13}$$

By differentiating eq 12 and setting $\Delta\theta$ equal to zero, we have

$$0 = \cos\frac{\tau}{2}\cos\frac{\phi}{2}\Delta\phi - \sin\frac{\tau}{2}\sin\frac{\phi}{2}\Delta\tau \tag{14}$$

or

$$\frac{\Delta\tau}{\Delta\phi} = \cot\frac{\phi}{2}\cot\frac{\tau}{2} \tag{15}$$

corresponding to eq 5.

The intramolecular potential energy V of the simple valence-force-field type is written for simplicity as

$$V = \tfrac{1}{2}(K_r\Delta r^2 + H_\phi\Delta\phi^2 + F_\tau\Delta\tau^2) \tag{16}$$

For the bond length r, from eq 7, we have

$$\frac{\partial V}{\partial r} = \frac{\partial V}{\partial d}\frac{\partial d}{\partial r} \tag{17}$$

where the summation in eq 7 is not needed because the variable r is not contained in eq 12 ($\partial\theta/\partial r = 0$). From eq 13, 16, and 17 and the relation of $\partial V/\partial d = f$,

$$K_r\Delta r = f\frac{d}{r} \tag{18}$$

For the bond angle ϕ, which is not independent of τ as understood from eq 15, we have

$$\frac{\partial V}{\partial \phi} + \frac{\partial V}{\partial \tau}\frac{\partial \tau}{\partial \phi} = \frac{\partial V}{\partial d}\left(\frac{\partial d}{\partial \phi} + \frac{\partial d}{\partial \tau}\frac{\partial \tau}{\partial \phi}\right) \tag{19}$$

By substituting eq 13, 15, and 16, eq 19 becomes the following form.

$$H_\phi\Delta\phi + F_\tau\cot\frac{\tau}{2}\cot\frac{\phi}{2}\Delta\tau = f\frac{d}{2}\cot\frac{\phi}{2}\Big/\sin^2\frac{\tau}{2} \tag{20}$$

The solution set to the simultaneous eq 15, 18, and 20 is as follows.

$$\begin{aligned} \Delta r &= fd/(K_r r) \\ \Delta\phi &= fd\sin\phi/(2N) \\ \Delta\tau &= fd\cos^2\frac{\phi}{2}\cot\frac{\tau}{2}\Big/N \end{aligned} \tag{21}$$

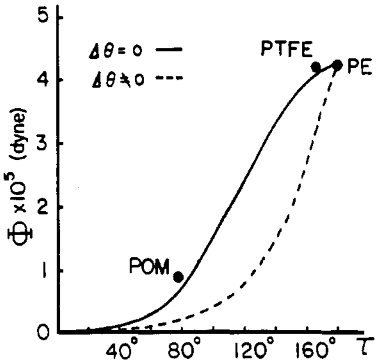


Figure 2. Comparison of tensile force Φ for $\Delta\theta = 0$ and for $\Delta\theta \neq 0$. ● represents the observed value.[11]

where

$$N = 2\left(H_\phi\sin^2\frac{\phi}{2}\sin^2\frac{\tau}{2} + F_\tau\cos^2\frac{\phi}{2}\cos^2\frac{\tau}{2}\right)$$

By substituting eq 21 into eq 4, we obtain Δd, from which we can calculate the elastic modulus E in eq 1.

In the case of $\Delta\theta \neq 0$, r, ϕ, and τ are all independent of each other, i.e., $\partial\tau/\partial\phi = 0$. Hence the following equations are obtained instead of eq 19.

$$\frac{\partial V}{\partial \phi} = \frac{\partial V}{\partial d}\frac{\partial d}{\partial \phi}$$

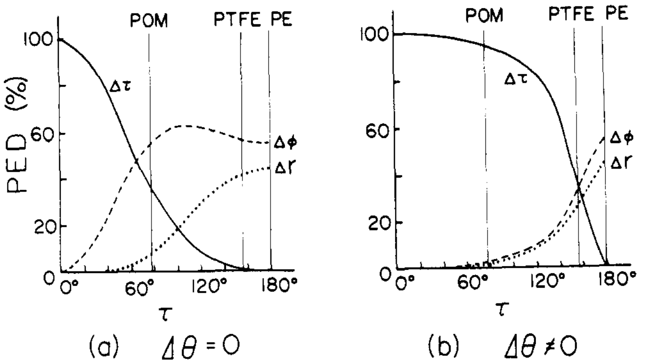
$$\frac{\partial V}{\partial \tau} = \frac{\partial V}{\partial d}\frac{\partial d}{\partial \tau}$$

Then we obtain the following equations which coincide with the equations derived by Shimanouchi et al.[5]

$$\begin{aligned} \Delta r &= fd/(K_r r) \\ \Delta\phi &= fd\cot\frac{\phi}{2}\Big/(2H_\phi) \\ \Delta\tau &= fd\cot\frac{\tau}{2}\Big/(2F_\tau) \end{aligned} \tag{22}$$

Figure 2 shows the tensile force Φ necessary to stretch the chain by 1% ($\Phi = EA \times 0.01$), as a function of the internal rotation angle τ, obtained by assuming the bond length r = 1.54 Å, the bond angle ϕ = 109.5°, and force constants K_r = 5 mdyn/Å, H_ϕ = 1.2 mdyn Å/rad^2, and F_τ = 0.09 mdyn Å/rad^2. The observed values (denoted by ●)[11] agree well with the calculated results for $\Delta\theta = 0$ (solid line). Hence we can understand the condition of $\Delta\theta = 0$ to be indispensable to the calculations of the elastic moduli in the chain direction.

Figure 3 shows PED to Δr, $\Delta\phi$, and $\Delta\tau$ as a function of τ, calculated from eq 10 for the above model: (a) for $\Delta\theta = 0$ and (b) for $\Delta\theta \neq 0$. For polyethylene (PE), PED's are about 50% to Δr and $\Delta\phi$ and 0% to $\Delta\tau$, respectively, in the cases of (a) and (b), since PE is all trans and so the internal rotations do not contribute to the stretching of the chain. In the case of $\Delta\theta = 0$, for the (15/7) helix of polytetrafluoroethylene (PTFE), PED to $\Delta\tau$ is almost 0%, and PED's to Δr and $\Delta\phi$ are nearly equal to those for PE. This similarity may be due to the conformation (τ = 166°) of PTFE not so much deviated from the planar zigzag. On the contrary, for polyoxymethylene (POM), PED to Δr is remarkably small and PED to $\Delta\tau$ large, which may be due to the fact that POM is the helix of nearly gauche sequences quite different from the planar zigzag.[12] It should be noted here that PED's of the above polymers (except PE) vary according to the condition of $\Delta\theta = 0$ or $\Delta\theta \neq 0$. Under the condition of $\Delta\theta \neq 0$, PED's to Δr and $\Delta\phi$ are lower and PED to $\Delta\tau$ higher than those under $\Delta\theta = 0$, which results in smaller values of tensile force Φ than those for $\Delta\theta = 0$. But the condition of $\Delta\theta \neq 0$ should not occur in the crystal lattice, as stated



(a) $\Delta\theta = 0$ (b) $\Delta\theta \neq 0$

Figure 3. Potential energy distributions under the condition of (a) $\Delta\theta = 0$ and (b) $\Delta\theta \neq 0$ for $(\text{-A-})_n$ type helices as a function of internal rotation angle τ.

above. The bond length r of POM is actually 1.43 Å, different from 1.54 Å used in the above calculations. But in the case of POM the contribution of the bond length to the elastic modulus is very small as can be understood from PED to Δr. Therefore we may discuss POM and the other polymers together in Figures 2 and 3.

General Types of Helices

Calculations of $\partial d/\partial R_i$ and Condition of $\Delta\theta = 0$. (A) Polymer Chains with Helical Symmetry ($\theta \neq 0$). For the general types of helices, the equations of helical parameters[10] are given by

$$d = \frac{c_1(a_{13} + a_{31}) + c_2(a_{23} + a_{32}) + c_3(1 - a_{11} - a_{22} + a_{33})}{2(1 - a_{11} - a_{22} + a_{33})^{1/2} \sin(\theta/2)} \tag{23}$$

$$\cos(\theta/2) = (1 + a_{11} + a_{22} + a_{33})^{1/2}/2 \tag{24}$$

where $a_{11}, a_{12}, \ldots, c_1, c_2$, and c_3 are given by

$$\mathbf{A} = \begin{bmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{bmatrix}$$

$$= \mathbf{A}^{\tau}{}_{1,2}\mathbf{A}^{\phi}{}_{2}\mathbf{A}^{\tau}{}_{2,3}\mathbf{A}^{\phi}{}_{3} \ldots \mathbf{A}^{\tau}{}_{p,p+1}\mathbf{A}^{\phi}{}_{p+1} \tag{25}$$

$$\mathbf{C} = \begin{bmatrix} c_1 \\ c_2 \\ c_3 \end{bmatrix} = \sum_{i=2}^{p} \mathbf{A}^{\tau}{}_{1,2}\mathbf{A}^{\phi}{}_{2} \ldots \mathbf{A}^{\tau}{}_{i-1,i}\mathbf{A}^{\phi}{}_{i}\mathbf{B}_{i,i+1} + \mathbf{B}_{1,2} \tag{26}$$

p is the number of main chain atoms in one asymmetric unit, and $\mathbf{A}^{\tau}{}_{i-1,i}$, $\mathbf{A}^{\phi}{}_{i}$, and $\mathbf{B}_{i-1,i}$ are expressed in terms of the bond length $r_{i-1,i}$, bond angle ϕ_i, and internal rotation angle $\tau_{i-1,i}$ as follows; i referring to the numbering of the main chain atoms.

$$\mathbf{A}^{\tau}{}_{i-1,i} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & \cos\tau_{i-1,i} & -\sin\tau_{i-1,i} \\ 0 & \sin\tau_{i-1,i} & \cos\tau_{i-1,i} \end{bmatrix}$$

$$\mathbf{A}^{\phi}{}_{i} = \begin{bmatrix} -\cos\phi_i & -\sin\phi_i & 0 \\ \sin\phi_i & -\cos\phi_i & 0 \\ 0 & 0 & 1 \end{bmatrix} \tag{27}$$

$$\mathbf{B}_{i-1,i} = \begin{bmatrix} r_{i-1,i} \\ 0 \\ 0 \end{bmatrix}$$

$\partial d/\partial R_i$ in eq 4 can be obtained by differentiating eq 23 with respect to R_i under the condition of constant θ. For this purpose, we must have $\partial a_{kl}/\partial R_i$ and $\partial c_m/\partial R_i$, which can be calculated from the differentiation of the elements in eq 25 and 26 with respect to R_i as follows.

$$\frac{\partial\mathbf{A}}{\partial\phi_i} = \mathbf{A}^{\tau}{}_{1,2}\mathbf{A}^{\phi}{}_{2} \ldots \mathbf{A}^{\tau}{}_{i-1,i}\left(\frac{\partial\mathbf{A}^{\phi}{}_{i}}{\partial\phi_i}\right)\mathbf{A}^{\tau}{}_{i+1,i} \ldots \mathbf{A}^{\phi}{}_{p+1}$$

$$\frac{\partial\mathbf{A}}{\partial\tau_{i-1,i}} = \mathbf{A}^{\tau}{}_{1,2}\mathbf{A}^{\phi}{}_{2} \ldots \mathbf{A}^{\phi}{}_{i-1}\left(\frac{\partial\mathbf{A}^{\tau}{}_{i-1,i}}{\partial\tau_{i-1,i}}\right)\mathbf{A}^{\phi}{}_{i} \ldots \mathbf{A}^{\phi}{}_{p+1}$$

$$\frac{\partial\mathbf{C}}{\partial\phi_i} = \sum_{k=i}^{p} \mathbf{A}^{\tau}{}_{1,2}\mathbf{A}^{\phi}{}_{2} \ldots \mathbf{A}^{\tau}{}_{i-1,i} \times \left(\frac{\partial\mathbf{A}^{\phi}{}_{i}}{\partial\phi_i}\right)\mathbf{A}^{\tau}{}_{i,i+1} \ldots \mathbf{A}^{\tau}{}_{k-1,k}\mathbf{A}^{\phi}{}_{k}\mathbf{B}_{k,k+1} \tag{28}$$

$$\frac{\partial\mathbf{C}}{\partial\tau_{i-1,i}} = \sum_{k=i}^{p} \mathbf{A}^{\tau}{}_{1,2}\mathbf{A}^{\phi}{}_{2} \ldots \mathbf{A}^{\tau}{}_{i-1} \times \left(\frac{\partial\mathbf{A}^{\tau}{}_{i-1,i}}{\partial\tau_{i-1,i}}\right)\mathbf{A}^{\phi}{}_{i} \ldots \mathbf{A}^{\tau}{}_{k-1,k}\mathbf{A}^{\phi}{}_{k}\mathbf{B}_{k,k+1}$$

$$\frac{\partial\mathbf{C}}{\partial r_{i-1,i}} = \mathbf{A}^{\tau}{}_{1,2}\mathbf{A}^{\phi}{}_{2} \ldots \mathbf{A}^{\tau}{}_{i-1,i}\mathbf{A}^{\phi}{}_{i}\mathbf{S}$$

$$\frac{\partial\mathbf{C}}{\partial r_{1,2}} = \mathbf{S} = \begin{bmatrix} 1 \\ 0 \\ 0 \end{bmatrix}$$

where

$$\frac{\partial\mathbf{A}^{\phi}{}_{i}}{\partial\phi_i} = \begin{bmatrix} \sin\phi_i & -\cos\phi_i & 0 \\ \cos\phi_i & \sin\phi_i & 0 \\ 0 & 0 & 0 \end{bmatrix}$$

$$\frac{\partial\mathbf{A}^{\tau}{}_{i-1,i}}{\partial\tau_{i-1,i}} = \begin{bmatrix} 0 & 0 & 0 \\ 0 & -\sin\tau_{i-1,i} & -\cos\tau_{i-1,i} \\ 0 & \cos\tau_{i-1,i} & -\sin\tau_{i-1,i} \end{bmatrix} \tag{29}$$

By differentiating eq 24 and setting $\Delta\theta$ equal to zero, we have eq 30 corresponding to eq 5.

$$0 = \Delta a_{11} + \Delta a_{22} + \Delta a_{33} \tag{30}$$

Since eq 30 is the sum of infinitesimal changes of the diagonal elements of eq 25, eq 30 can be expressed in terms of the bond angles and internal rotation angles as follows.

$$0 = \sum_{i=2}^{p+1}\left(\operatorname{trace}\frac{\partial\mathbf{A}}{\partial\phi_i}\right)\Delta\phi_i + \sum_{i=2}^{p+1}\left(\operatorname{trace}\frac{\partial\mathbf{A}}{\partial\tau_{i-1,i}}\right)\Delta\tau_{i-1,i} \tag{31}$$

(B) Polymer Chains with only Translational Symmetry. The fiber identity period d is given as follows by using eq 26.

$$d = (c_1^2 + c_2^2 + c_3^2)^{1/2} = (\tilde{\mathbf{C}}\mathbf{C})^{1/2} \tag{32}$$

Then

$$\frac{\partial d}{\partial R_i} = \sum_{k=1}^{3}\frac{\partial d}{\partial c_k}\frac{\partial c_k}{\partial R_i} = \sum_k \frac{c_k}{d}\frac{\partial c_k}{\partial R_i} = \frac{\tilde{\mathbf{C}}(\partial\mathbf{C}/\partial R_i)}{d} \tag{33}$$

where $\partial\mathbf{C}/\partial R_i$ is given by eq 28 and a tilde denotes transposed vector.

The condition of $\Delta\theta = 0$ is represented by eq 31.

Calculation of Elastic Moduli

In addition to the condition of eq 5 we should take into account the redundant conditions, which may be represented as follows.

$$\sum_i W_{mi}\Delta R_i = 0 \qquad (m = 1, 2, \ldots, M) \tag{34}$$

Table I
Molecular Parameters of Isotactic Polypropylene

Bond length C–C, Å	1.54
Bond angle ∠CCC, deg	114.0
Internal rotation angles, deg	180.0 and −60.0
Effective cross-sectional area, $Å^2$	34.39
Force constants	
CC stretching, mdyn/Å	4.472
∠CCC bending, mdyn $Å/rad^2$	0.684
CCCC torsion, mdyn $Å/rad^2$	0.095
Interaction between CC and CC, mdyn/Å	0.138
Interaction between CC and ∠CCC, mdyn/rad	0.404
Interaction between ∠CCC and ∠CCC, mdyn $Å/rad^2$	0.099

where W_{mi} is the coefficient and M is the number of redundant conditions per asymmetric unit. The summation is made over the coordinates relating to each redundant condition.

Equations 5, 9, and 34 can be represented by matrices en bloc;

$$\begin{bmatrix} \mathbf{H} & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & \mathbf{E} \end{bmatrix} \begin{bmatrix} \mathbf{F_R} \\ \mathbf{U} \\ \mathbf{W} \end{bmatrix} \Delta\mathbf{R} = f \begin{bmatrix} \mathbf{H} \\ 0 \\ 0 \end{bmatrix} \mathbf{J_R} \qquad (35)$$

where

$$\mathbf{H} = \begin{bmatrix} \dfrac{\partial R_1}{\partial R_1} & \cdots & \dfrac{\partial R_n}{\partial R_1} \\ \vdots & \cdots & \vdots \\ \dfrac{\partial R_1}{\partial R_q} & \cdots & \dfrac{\partial R_n}{\partial R_q} \end{bmatrix}$$

$$\mathbf{F_R} = \begin{bmatrix} F_{11} & \cdots & F_{1n} \\ \vdots & \cdots & \vdots \\ F_{n1} & \cdots & F_{nn} \end{bmatrix}$$

$$\mathbf{U} = \begin{bmatrix} \dfrac{\partial\theta}{\partial R_1} & \dfrac{\partial\theta}{\partial R_2} & \cdots & \dfrac{\partial\theta}{\partial R_n} \end{bmatrix}$$

$$\mathbf{W} = \begin{bmatrix} W_{11} & \cdots & W_{1n} \\ \vdots & \cdots & \vdots \\ W_{M1} & \cdots & W_{Mn} \end{bmatrix}$$

$$\tilde{\mathbf{J}}_{\mathbf{R}} = \begin{bmatrix} \dfrac{\partial d}{\partial R_1} & \dfrac{\partial d}{\partial R_2} & \cdots & \dfrac{\partial d}{\partial R_n} \end{bmatrix}$$

$$\mathbf{E} = \begin{bmatrix} 1 & & 0 \\ & 1 & \\ & & \ddots \\ 0 & & 1 \end{bmatrix}$$

$$\Delta\tilde{\mathbf{R}} = [\Delta R_1 \quad \Delta R_2 \quad \dots \quad \Delta R_n\}$$

n is the total number of variables taken into account and q is the number of independent variables ($q = n - M - 1$). The quantity $\partial R_s/\partial R_t$ in the matrix **H** is obtained by using eq 31 and 34 as follows.

$$\frac{\partial R_j}{\partial R_i} = \begin{cases} 1 & (i = j) \\ 0 & (i \neq j) \end{cases}$$

$$\frac{\partial R_k}{\partial R_i} = -\frac{(\partial\theta/\partial R_i)}{(\partial\theta/\partial R_k)} \text{ or } -\frac{W_{mi}}{W_{mk}}$$

where R_i and R_j are independent variables and R_k is dependent upon R_i. Equation 35 is a system of n-dimensional simultaneous equations to the all internal displacement coordinates, which can be easily solved by the sweep-out method, etc. Δd in eq 4 is calculated by the solution set $\Delta\mathbf{R}$ thus obtained, and then the elastic modulus E is given in eq 1.

As examples, E were calculated for isotactic polypropylene (it-PP) (3/1) helix (consisting of only skeletal chain atoms) and poly(vinylidene fluoride) (PVDF) forms I and II. PVDF forms I and II were treated as polymers with only translational symmetry. The parameters used are shown in Table I for it-PP[13] and in ref 14 and 15 for PVDF. The calculated results are listed in Table II in comparison with the observed ones. Figure 4 shows the potential energy distributions for these polymers. The calculated elastic moduli of it-PP and PVDF form II show fairly good agreements with the observed values. For PVDF form II, PED to the internal rotation angles of the gauche C–C bonds is 30%, while that of the trans bonds is nearly zero. The situation for it-PP, however, is just of the opposite sense. It should be noted that PED to the gauche C–C bonds of it-PP has a nonzero value under the condition of $\Delta\theta = 0$, different from the case of $\Delta\theta \neq 0$ (Table III), although the gauche bonds are parallel to the fiber axis before stretching. It is of interest that the deformation mechanisms of the similar local structures differ according to the difference in the whole chain conformation, helix or glide; the reason will be discussed in detail in a later section. When the polymer chain of PVDF form II is stretched as shown in Figure 4, the internal rotation angles G and $\overline{G}$ tend to rotate in the direction of trans so that the conformation becomes closer to the planar zigzag (form I). PVDF form II is transformed to form I by cold-drawing or by heat-treatment under high pressure,[16] which may be related to the above mechanism of deformation.

The calculated Φ value of PVDF form I is 4.89×10^{-5} dyn, which is in the range of the values observed for the planar zigzag polymers (PE, 4.28×10^{-5} dyn; poly(vinyl alcohol), 5.40×10^{-5} dyn).[11] But the observed Φ value for PVDF form I is 3.65×10^{-5} dyn,[11] considerably smaller than the expected values for planar zigzag chains. We previously proposed a model of molecular conformation of PVDF form I alternately deflected on the right and left sides from the planar zigzag, based upon the results of x-ray structure analysis,[14] energy calculation,[16] and vibrational spectra.[15] The alternately deflected chain molecule with the deflection angle 14°, for example, as proposed by x-ray analysis (Figure 4),[14] gives the calculated Φ value of 4.62×10^{-5} dyn, which is to some extent smaller than that of the planar zigzag chain. Therefore the

Table II
Crystallite Moduli of it-PP and PVDF Forms I and II

	Crystallite modulus, dyn/cm^2		Tensile force Φ, dyn	
Polymer	Obsd[11]	Calcd	Obsd[11]	Calcd
it-PP (3/1)	34×10^{10}	25×10^{10}	1.18×10^{-5}	1.60×10^{-5}
PVDF form I				
Planar zigzag chain	177	237		4.89
Deflected chain		224	3.65	4.62
PVDF form II	59	77	1.52	1.98

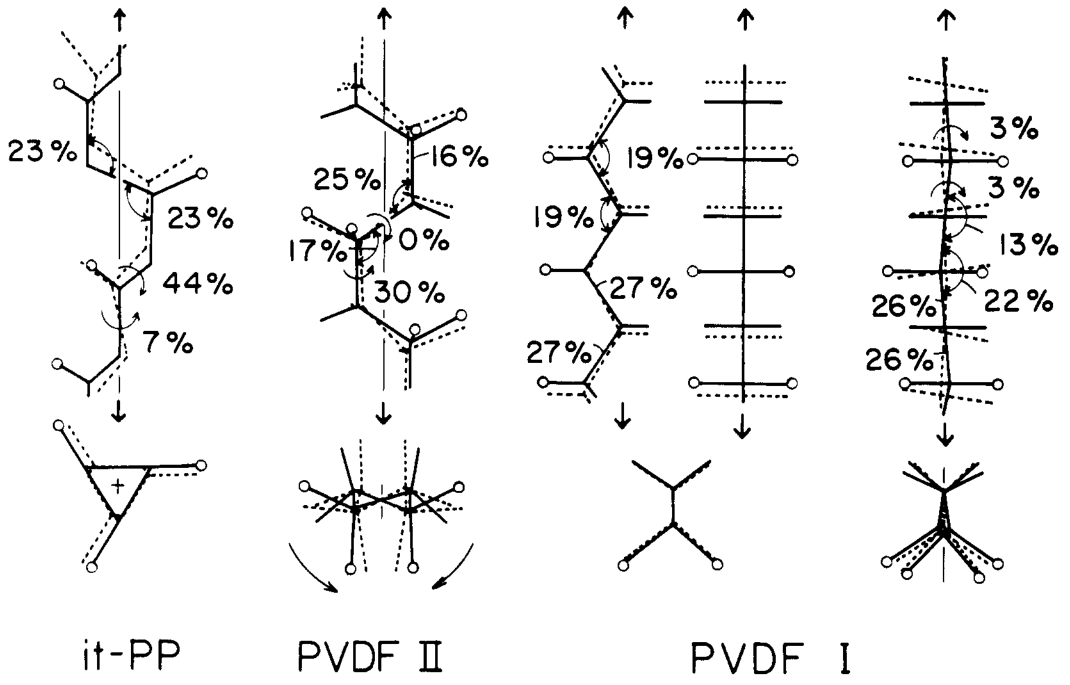


Figure 4. Potential energy distributions for it-PP and PVDF forms I (planar zigzag chain and deflected chain models) and II under the condition of $\Delta\theta = 0$. Broken lines represent the conformations deformed by a hypothetically large strain of 10%.

Table III
Potential Energy Distributions to Internal Rotation Angles and Their Geometrical Factors $(\partial d/\partial R_i)^2$ for it-PP and PVDF Form II

	it-PP		PVDF form II	
	$\tau(\mathrm{G})^a$	$\tau(\mathrm{T})$	$\tau(\mathrm{G})$	$\tau(\mathrm{T})$
PED($\Delta\theta = 0$)	7.3%	44.3%	30.0%	0.04%
PED($\Delta\theta \neq 0$)	0.00%	72.1%	23.1%	22.1%
$(\partial d/\partial R_i)^{2b}$	0.00	0.07	0.011	0.010

[a] $\tau(\mathrm{G})$ and $\tau(\mathrm{T})$ represent the internal rotation angles of gauche C–C bonds and trans C–C bonds, respectively. [b] $(\partial d/\partial R_i)^2$ is dimensionless (see text).

deflection of chain may be one of the reasons why PVDF form I has the small Φ value.

Factors Governing the Elastic Moduli and Potential Energy Distributions

If the constraining conditions of eq 5 ($\Delta\theta = 0$) and eq 34 (redundant conditions) are neglected, eq 35 is reduced to the equation derived by Shimanouchi et al.[5]

$$\Delta\tilde{\mathbf{R}} \simeq f(\mathbf{F_R})^{-1}\mathbf{J_R}$$

or

$$\Delta R_i \simeq f \sum_k (\partial d/\partial R_k)F_{ik}^{-1} \simeq f(\partial d/\partial R_i)F_{ii}^{-1} \qquad (36)$$

where the off-diagonal elements of the inversed matrix of force constants are neglected. Therefore PED in eq 10 can be written approximately as follows.

$$(\mathrm{PED})_i = NF_{ii}\Delta R_i^2 \simeq N'(\partial d/\partial R_i)^2F_{ii}^{-1} \qquad (37)$$

By using eq 4 and 36, the elastic modulus E in eq 1 is expressed as

$$E = (fd/A)/\Delta d = (fd/A)\Big/\sum_i (\partial d/\partial R_i)\Delta R_i$$
$$\simeq N''\Big/\sum_i (\partial d/\partial R_i)^2F_{ii}^{-1} \simeq N'''\Big/\sum_i (\mathrm{PED})_i \qquad (38)$$

Here N, N', N'', and N''' are constants. As shown in eq 37, the PED to the ith internal displacement coordinate ΔR_i is approximately proportional to $(\partial d/\partial R_i)^2$ and inversely proportional to F_{ii}. That is, the more effectively the pitch d varies with R_i, the higher the PED to ΔR_i. And the more flexible is R_i, the higher the PED to ΔR_i. The elastic modulus E is proportional to the reciprocal of $\Sigma_i(\mathrm{PED})_i$. Since $\Sigma_i(\mathrm{PED})_i$ is mainly governed by some members of $(\mathrm{PED})_i$'s having large values, we can obtain an important conclusion that the modulus E is practically determined by the geometrical factor $(\partial d/\partial R_i)^2$ and the flexibility F_{ii}^{-1} of the internal coordinates having the large PED.

Application of this consideration to poly(ethylene oxybenzoate) α form and poly(m-phenylene isophthalamide) has been described in the previous paper.[17] Poly(ethylene oxybenzoate) α form, which takes the conformation of a large scale zigzag, one monomeric unit being one zigzag unit,[18] has the very low crystallite modulus 6×10^{10} dyn/cm^2.[11] The strain energy distributes almost to the internal rotation angle τ_{12}, about 70% (Figure 5), because the helical pitch d is elongated sensitively by the change of τ_{12} ($\partial d/\partial\tau_{12}$ is large), and the force constant of τ_{12} is very small compared with those of the other internal coordinates (flexibility $F_{\tau_{12}}^{-1}$ is large). Thus we can say that the small value of the crystallite modulus E of this polymer originates in the two factors, that is, the long length of the arm (about 6 Å, much larger than the value of 0.9 Å in PE) of the component of the moment of force and the small values of the internal rotation force constants.

In the previous section we indicated the difference in PED between it-PP and PVDF form II, which is now discussed by the two factors described above. In Table III are compared the PED to $\tau(\mathrm{G})$ and $\tau(\mathrm{T})$ under the conditions of $\Delta\theta = 0$ and $\Delta\theta \neq 0$ for both polymers. For it-PP, PED to $\tau(\mathrm{G})$ is small under both conditions, 0% for $\Delta\theta \neq 0$ and about 7% for $\Delta\theta = 0$, while PED to $\tau(\mathrm{T})$ is much larger. These PED's can be expected from the relation of $(\partial d/\partial\tau(\mathrm{G}))^2 \ll (\partial d/\partial\tau(\mathrm{T}))^2$ as shown in Table III. The flexibilities of $\tau(\mathrm{G})$ and $\tau(\mathrm{T})$ may be considered to be equal to each other, because the internal rotation force constants are assumed to be common to both internal rotation angles. For PVDF form II, $(\partial d/\partial\tau(\mathrm{G}))^2 \simeq (\partial d/\partial\tau(\mathrm{T}))^2$ and therefore PED to $\tau(\mathrm{T})$ should be nearly equal to that of $\tau(\mathrm{G})$

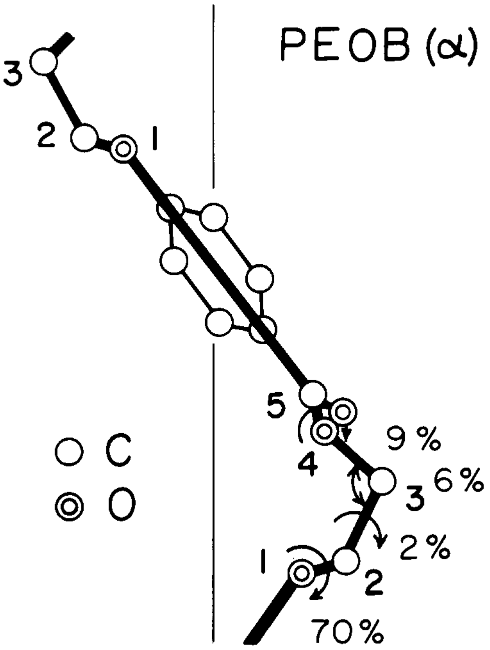


Figure 5. Potential energy distributions for poly(ethylene oxybenzoate) α form. The bold line represents the model used in calculation.

as expected from the approximated eq 37, where the condition of $\Delta\theta = 0$ is neglected. In fact, PED to τ(G) and τ(T) have almost the same values without the condition of $\Delta\theta = 0$, as shown in Table III. But under the condition of $\Delta\theta = 0$, PED to τ(T) is nearly zero. From eq 31 the condition of $\Delta\theta = 0$ is expressed by

$$\Delta\phi_1 - \Delta\phi_2 + 2.1\Delta\tau(\mathrm{T}) = 0 \qquad (39)$$

where $\phi_1 = \angle CH_2\text{–}CF_2\text{–}CH_2$ and $\phi_2 = \angle CF_2\text{–}CH_2\text{–}CF_2$. $\Delta\phi_1$ and $\Delta\phi_2$ are calculated to have values of the same order, so that $\Delta\tau$(T) becomes very small using eq 39, resulting in the nearly zero PED. $\Delta\tau$(G) has high PED as expected from the large value of $(\partial d/\partial\tau(\mathrm{G}))^2$ in Table III, since $\Delta\tau$(G) is an independent variable. Thus the very small PED to τ(T) in Figure 4 may be due to the existence of the condition of $\Delta\theta = 0$, unexpected from eq 37. As described above, eq 37 and 38 are very useful for the discussion of the elastic deformations of the chains. We must, however, remember that these equations have some limitations because of neglecting the condition of $\Delta\theta = 0$, when we discuss the potential energy distributions of chains in the "crystal lattice", as found in the case of PVDF form II.

In the above discussion, $(\partial d/\partial R_i)^2$ is dimensionless and the unit of F_{ii}^{-1} is mdyn/Å. Such dimensions were adjusted for the bond angles (indicated by the atoms i, j, and k) and internal rotation angles (indicated by the atoms i, j, k, and l) according to the following equations.

$$\partial d/\partial\phi(\text{dimensionless}) = \partial d/\partial\phi(\text{Å/rad})/(r_{ij}r_{jk})^{1/2}$$

$$\partial d/\partial\tau(\text{dimensionless}) = \partial d/\partial\tau(\text{Å/rad})/(r_{ij}r_{kl}\sin\phi_{ijk}\sin\phi_{jkl})^{1/2}$$

$$F_\phi^{-1}(\text{Å/mdyn}) = F_\phi^{-1}(\text{rad}^2/\text{mdyn Å})r_{ij}r_{jk}$$

$$F_\tau^{-1}(\text{Å/mdyn}) = F_\tau^{-1}(\text{rad}^2/\text{mdyn Å})r_{ij}r_{kl}\sin\phi_{ijk}\sin\phi_{jkl}$$

References and Notes

(1) K. H. Meyer and W. Lotmar, *Helv. Chim. Acta*, **19**, 68 (1935).
(2) H. Mark, *Trans. Faraday Soc.*, **32**, 144 (1936).
(3) W. J. Lyons, *J. Appl. Phys.*, **29**, 1429 (1958); **30**, 796 (1959).
(4) L. R. G. Treloar, *Polymer*, **1**, 95, 279, 290 (1960).
(5) T. Shimanouchi, M. Asahina, and S. Enomoto, *J. Polym. Sci.*, **57**, 93 (1962).
(6) M. Asahina and S. Enomoto, *J. Polym. Sci.*, **59**, 101 (1962).
(7) S. Enomoto and M. Asahina, *J. Polym. Sci.*, **59**, 113 (1962).
(8) H. Sugeta and T. Miyazawa, *Polym. J.*, **1**, 226 (1970).
(9) T. R. Manley and C. G. Martin, *Polymer*, **14**, 632 (1973).
(10) T. Miyazawa, *J. Polym. Sci.*, **55**, 215 (1961).
(11) I. Sakurada and K. Kaji, *J. Polym. Sci., Part C*, **31**, 57 (1970).
(12) T. Uchida and H. Tadokoro, *J. Polym. Sci., Part A-2*, **5**, 63 (1967).
(13) R. G. Snyder and G. Zerbi, *Spectrochim. Acta*, **23a**, 391 (1971).
(14) R. Hasegawa, Y. Takahashi, Y. Chatani, and H. Tadokoro, *Polym. J.*, **3**, 600 (1972).
(15) M. Kobayashi, K. Tashiro, and H. Tadokoro, *Macromolecules*, **8**, 158 (1975).
(16) R. Hasegawa, M. Kobayashi, and H. Tadokoro, *Polym. J.*, **3**, 591 (1972).
(17) K. Tashiro, M. Kobayashi, and H. Tadokoro, *Macromolecules*, **10**, 413 (1977).
(18) H. Kusanagi, H. Tadokoro, and Y. Chatani, *Macromolecules*, **10**, 405 (1977).

Brillouin Scattering from Molten Linear Polyethylene

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ABSTRACT: Brillouin scattering from several molten linear polyethylenes is examined. The master relation between phonon velocity and relative free volume given by Champion and Jackson is extended and confirmed. A more general relation is used to examine in detail the phonon velocity and conclusions are drawn about the local structure in polyethylene melts.

Brillouin scattering from liquid n-alkanes has been extensively studied by Champion and Jackson.[1] A master relation between longitudinal phonon velocity V_l and relative free volume, V_0/V_f, where V_0 is the specific volume extrapolated to 0 K without chnge of phase and V_f is the free volume

$$V_l \propto (V_0/V_f)^{1/3} \qquad (1)$$

was found to hold for the n-alkanes in the temperature range 20–140 °C. Also, the phonon velocity at each temperature appeared to be approaching an asymptote with chain length. The present work extends the measurements of V_l to include higher molecular weight polyethylenes in the molten state. The results are then discussed in terms of the general theory of sound velocity in liquids. Conclusions are also drawn about the nature of molten linear polyethylene.

Theory

Longitudinal thermal acoustic phonons interact with light to give frequency shifted scattered light with splitting